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**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

IN RE APPLICATION OF: Bernhard MOHR et al.
SERIAL NO.: NEW U.S. PCT APPLICATION
FILED: HEREWITH
INTERNATIONAL APPLICATION NO.: PCT/EP00/04293
INTERNATIONAL FILING DATE: May 12, 2000
FOR: ALKOXYLATED, CONDENSED BASIC AMINO ACID-CONTAINING POLYMERS AND THEIR PRODUCTION

**REQUEST FOR PRIORITY UNDER 35 U.S.C. 120 AND THE INTERNATIONAL CONVENTION**

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

In the matter of the above-identified application for patent, notice is hereby given that the applicant claims as priority:

| COUNTRY | APPLICATION NO | DAY/MONTH/YEAR |
|---|---|---|
| USA | 09/314,116 | 19 May 1999 |

Certified copies of the corresponding Convention application(s) were submitted to the International Bureau in PCT Application No. PCT/EP00/04293. Receipt of the certified copy(s) by the International Bureau in a timely manner under PCT Rule 17.1(a) has been acknowledged as evidenced by the attached PCT/IB/304.

Respectfully submitted,
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PCT/EP00/04293
09/926,568

EP00/04293

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# THE UNITED STATES OF AMERICA

TO ALL TO WHOM THESE PRESENTS SHALL COME:

UNITED STATES DEPARTMENT OF COMMERCE

United States Patent and Trademark Office

February 17, 2000

THIS IS TO CERTIFY THAT ANNEXED HERETO IS A TRUE COPY FROM THE RECORDS OF THE UNITED STATES PATENT AND TRADEMARK OFFICE OF THOSE PAPERS OF THE BELOW IDENTIFIED PATENT APPLICATION THAT MET THE REQUIREMENTS TO BE GRANTED A FILING DATE UNDER 35 USC 111.

APPLICATION NUMBER: *09/314,116*
FILING DATE: *May 19, 1999*

**PRIORITY DOCUMENT**
SUBMITTED OR TRANSMITTED IN COMPLIANCE WITH RULE 17.1(a) OR (b)

By Authority of the
COMMISSIONER OF PATENTS AND TRADEMARKS

T. LAWRENCE
Certifying Officer

# UTILITY - PATENT APPLICATION TRANSMITTAL

*(Only for new nonprovisional applications under 37 CFR 1.53(b))*

| | |
|---|---|
| Attorney Docket No. | 0524-3123-0 |
| First Inventor or Application Identifier | Bernhard MOHR, et al. |
| Title | ALKOXYLATED, CONDENSED BASIC AMINO ACID-CONTAINING POLYMERS AND A PROCESS FOR THEIR PRODUCTION |

09/314116 U.S. PTO 05/19/99

## APPLICATION ELEMENTS

*See MPEP chapter 600 concerning utility patent application contents*

ADDRESS TO: Assistant Commissioner for Patents
Box Patent Application
Washington, DC 20231

09/314116 JC408 U.S. PTO 05/19/99

1. ■ Fee Transmittal Form (e.g. PTO/SB/17)
(Submit an original and a duplicate for fee processing)

2. ■ Specification — Total Pages: 21

3. □ Drawing(s) *(35 U.S.C. 113)* — Total Sheets:

4. □ Oath or Declaration — Total Pages:
   a. □ Newly executed (original or copy)
   b. □ Copy from a prior application *(37 C.F.R. §1.63(d))* *(for continuation/divisional with box 15 completed)*
      i. □ DELETION OF INVENTOR(S)
      Signed statement attached deleting inventor(s) named in the prior application, see *37 C.F.R §1.63(d)(2) and 1.33(b).*

5. □ Incorporation By Reference *(usable if box 4B is checked)*
The entire disclosure of the prior application, from which a copy of the oath or declaration is supplied under Box 4B, is considered to be part of the disclosure of the accompanying application and is hereby incorporated by reference therein

### ACCOMPANYING APPLICATION PARTS

6. □ Assignment Papers (cover sheet & document(s))
7. □ 37 C.F.R. §3.73(b) Statement *(when there is an assignee)* □ Power of Attorney
8. □ English Translation Document *(if applicable)*
9. □ Information Disclosure Statement (IDS)/PTO-1449 □ Copies of IDS Citations
10. □ Preliminary Amendment
11. ■ White Advance Serial No. Postcard
12. □ Small Entity Statement(s) □ Statement filed in prior application. Status still proper and desired.
13. □ Certified Copy of Priority Document(s) *(if foreign priority is claimed)*
14. ■ Other: List of Inventors' Names

15. If a CONTINUING APPLICATION, *check appropriate box, and supply the requisite information below.*
□ Continuation □ Divisional □ Continuation-in-part (CIP) of prior application no.:
*Prior application information:* Examiner: Group Art Unit:

16. Amend the specification by inserting before the first line the sentence:
□ This application is a □ Continuation □ Division □ Continuation-in-part (CIP)
of application Serial No. Filed on

□ This application claims priority of provisional application Serial No. Filed

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Registration Number 21,124

Docket No. 0524-3123-0

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

IN RE APPLICATION OF: Bernhard MOHR, et al.

FILING DATE: Herewith

FOR: ALKOXYLATED, CONDENSED BASIC AMINO ACID-CONTAINING POLYMERS AND A PROCESS FOR THEIR PRODUCTION

## LIST OF INVENTORS' NAMES

ASSISTANT COMMISSIONER FOR PATENTS
WASHINGTON, D.C. 20231

SIR:

Listed below are the names of the inventors for the above-identified patent application.

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Dieter BOECKH

Oliver BORZYK

A declaration containing all the necessary information will be submitted at a later date.

Respectfully Submitted,

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# Alkoxylated, condensed basic amino acid-containing polymers and a proce s for their production

## Description

### Technical Field

The present invention relates to alkoxylated, condensed basic amino acid-containing polymers and a process for their production.

### Background of the invention

Ethoxylated polyamines, especially polyethyleneimines and processes for their production are known, cf. U.S. Patent 3,313,736, U.S. Patent 4,891,160, U.S. Patent 4,551,506 and WO-A-97/23546. The ethoxylated polyamines are for example used in cleaning compositions.

DE-A-2 227 546 relates to the use of alkoxylated polyalkyleneimines for the dehydration of crude oils. The alkoxylated polyalkyleneimines are prepared by a two-stage process in which, in the first stage, 1 mole of an alkylene oxide, based on 1 mole of NH groups in the polyethyleneimine, is reacted with a polyalkylenepolyamine in the presence of water under formation of hydroxyalkyl groups. In the second process stage water is initially removed from the reaction mixture, an alkaline catalyst added, alkylene oxide forced in and the reaction carried out under pressure at temperatures between 125° and 135°C. From 10 to 300 alkylene oxide units are added per NH group. Alternatively, the alkoxylation can be carried out in a single stage, by forcing in alkylene oxide in the presence of aqueous or anhydrous alkaline catalysts and causing it to react under pressure with polyethyleneimines at temperatures between 125° and 135°C.

EP-A-0,112,593 relates to detergent formulations containing ethoxylated amines. In this case the preparation of the alkoxylated amines likewise takes place in two stages, a hydroxyethylated polyethyleneimine being produced in the first stage by the action of ethylene oxide and the necessary amount of ethylene oxide being added in the second stage by further addition of ethylene oxide at temperatures ranging from 130° to 140°C under super atmospheric pressure. The degree of ethoxylation is for example from 15 to 42.

WO-A-97/20879 relates to a process for the preparation of hydroxyalkylated polyethyleneimines by hydroxyalkylation of polyethyleneimines in one or two procedural stages to form reaction products which contain 1 to 200 mol alkylene oxide groups per NH group in the polyethyleneimine. In the one-stage process, there are anhydrous polyethyleneimines and 1 to 200 mol %, in relation to the polyethyleneimines, of at least one anhydrous base or aqueous solutions of said substances are dehydrated and after removing all the water are reacted at temperatures above 135 - 150°C with at least one alkylene oxide. Alternatively, in the two-stages process, in the first stage polyethyleneimine is reacted at temperatures from 80 to 100°C with 0.7 to 0.9 mol, in relation to one mol NH group in the polymerisate, of at least one alkylene oxide in an aqueous solution, and in the second stage the reaction product obtained in the first step is reacted in the presence of 1 to 20 mol %, in relation to polyethyleneimine, of an alkaline catalyst in the absence of water at temperatures from 120 to 150°C with at least one alkylene oxide to form hydroxyalkylated polyethyleneimines which contain 1 to 200 mol of alkylene oxide groups per NH group in the polyethyleneimine. The resulting alkoxylated products are only slightly coloured.

U.S. Application Serial No. 09/131,234 relates to an amino acid based polymer, oligomer or copolymer containing at least 5 mol % of units of a basic amino acid selected from the group consistig of lysine, arginine, ornithine, tryptophane and mixtures thereof and at least about 5 mol % of a polymerizable compound selected from the group consisting of aliphatic or cycloaliphatic amines, alicyclic amines, diamines, triamines, tetraamines, aliphatic amino alcohols or mixtures therof. The said polymers, oligomers or copolymers are obtained by condensing said basic amino acids at a temperature of at least 120°C said basic amino acids with at least one of said polymerizable compounds. The condensation products may be used as additive for detergents and/or other laundry additves.

U.S. Application Serial No. 09/131,282 relates to condensation products of basic amino acids with copolymerizable compounds which are obtained by condensing

(a) a basic amino acid selected from the group consisting of lysine, arginine, ornithine, tryptophane and mixtures thereof,

(b) a copolymerizable compound selected from the group consisting of saturated monobasic carboxylic acids, unsaturated monobasic carboxylic acids, polybasic carboxylic acids,

carboxylic acid anhydrides, diketenes, monohydroxycarboxylic acids, polyhydroxycarboxylic acids and mixtures thereof, and optionally

(c) at least one compound selected from the group consisting of amines, lactams, non-proteinogenic amino acids, alcohols, alkoxylated alcohols, alkoxylated amines, amino sugars, carbohydrates and sugar carboxylic acids

in a molar ratio of (a) : (b) of from 100 : 1 to 1 : 1 at a temperature of at least 120°C. The condensation products may be used as additive in detergents.

It is the object of the invention to provide new condensation products of basic amino acids.

Summary of the invention

The above object is achieved with alkoxylated, condensed basic amino acid-containing polymers comprising the addition products of alkylene oxides to

- homocondensates of basic amino acids,
- condensates of mixtures of two or more basic amino acids and
- cocondensates of basic amino acids and cocondensable compounds.

The object is also achieved with a process for the production of alkoxylated, condensed basic amino acid-containing polymers by reacting

- homocondensates of basic amino acids,
- condensates of mixtures of two or more basic amino acids and
- cocondensates of basic amino acids and cocondensable compounds

with at least one alkylene oxide selected from C2- to C30-alkylene oxides and styrene oxide. The alkoxylated, condensed basic amino acid-containing polymers may be used as additives for detergents.

Detailed description of the invention

In order to produce condensed basic amino acid-containing polymers basic amino acids are preferably condensed thermally. Other methods for the production of basic amino acid-containing polymers are based on chemical methods (e.g. via N-carboxy anhydrides

of the basic amino acids) or on microorganisms. Basic amino acids, which are hereinafter referred to as compounds of group (a), are lysine, arginine, ornithine, tryptophane and their mixtures. These compounds may be used in the form of their hydrates, their esters with lower alcohols or their salts, for instance their sulfates, hydrochlorides or acetates. The esters of the basic amino acids are preferably derived from monovalent C1 to C4-alcohols such as methanol, ethanol, n-propanol, isopropanol, n-butanol, sec.-butanol or tertiary butanol. When hydrochlorides are used, approximately equivalent quantities of a base should be added to the reaction mixture for neutralization of hydrogen chloride. Sodium hydroxide and potassium hydroxide are the preferred bases. If a monohydrochloride of a basic amino acid is used, one equivalent of a base is necessary whereas in case of dihydrochlorides two equivalents are required. Lysine hydrate and aqueous solutions of lysine are preferably used as basic amino acid. Lysine can also be used in form of its cyclic lactam, i.e. α-amino-ε-caprolactam.

Compounds which are cocondensable with basic amino acids are hereinafter referred to as compounds of group (b) for example compounds having at least one carboxyl group, carboxylic acid anhydrides, diketenes, amines, lactams, alcohols, alkoxylated alcohols and alkoxylated amines. Carboxyl group-containing compounds are for instance saturated monobasic carboxylic acids, unsaturated monobasic carboxylic acids, polybasic carboxylic acids, monohydroxycarboxylic acids, monobasic polyhydroxycarboxylic acids, non-proteinogenic amino acids and mixtures thereof. Examples of saturated monobasic carboxylic acids are formic acid, acetic acid, propionic acid, butyric acid, valeric acid, capric acid, octanoic acid, nonanoic acid, decanoic acid, lauric acid, palmitic acid, stearic acid, arachidic acid, behenic acid, myristic acid, undecanoic acid, 2-ethyl hexanoic acid, and all naturally occuring fatty acids and mixtures thereof.

Examples of unsaturated monobasic carboxylic acids are acrylic acid, methacrylic acid, crotonic acid, sorbic acid, oleic acid, linoleic acid, and erucic acid.

Examples of polybasic carboxylic acids are oxalic acid, fumaric acid, maleic acid, malonic acid, succinic acid, itaconic acid, adipic acid, aconitic acid, suberic acid, azeleic acid, pyridinedicarboxylic acid, furandicarboxylic acid, phthalic acid, terephthalic acid, diglycolic acid, glutaric acid, substituted C4-dicarboxylic acid, sulfosuccinic acid, C1- to C26-alkylsuccinic acids, C2- to C26-alkenylsuccinic acids, 1,2,3-propanetricarboxylic acids, 1,1,3,3-propanetetracarboxylic acids,

1,1,2,2-ethanetetracarboxylic acid, 1,2,3,4-butanetetracarboxylic acid, 1,2,2,3-propanetetracarboxylic acid, 1,3,3,5-pentanetetracarboxylic acid, 1,2,4-benzenetricarboxylic acid, and 1,2,4,5-benzenetetracarboxylic acid.

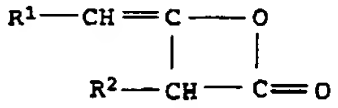
Examples of monohydroxycarboxylic acids are malic acid, tartronic acid, citric acid, and isocitric acid. Polyhydroxycarboxylic acids are for example tartaric acid, mucic acid, glyceric acid, bis(hydroxymethyl)propinonic acid, gluconic acid, and hydroxylated unsaturated fatty acids such as dihydroxystearic acid.

Other carboxyl group-containing compounds are non-proteinogenic amino acids. Examples of such acids are anthranilic acid, N-methylamino substituted acids such as N-methylglycine, dimethylaminoacetic acid, ethanolaminoacetic acid, N-carboxymethylamino acids, nitrilotriacetic acid, ethylenediamineacetic acid, ethylenediaminotetraacetic acid, diethylentriaminepentaacetic acid, hydroxyethylenediaminotriacetic acid, diaminosuccinic acid, C4- to C26-aminoalkylcarboxylic acids such as 4-aminobutyric acid, 6-aminocaproic acid, and 11-aminoundecanoic acid.

Other carboxyl group-containing compounds which differ form basic amino acids and α-amino acids and which can be condensed with basic amino acids are sugarcarboxylic acids such as gluconic acid, gluaric acid, gluconolactone, and glucuronic acid.

Carboxylic anhydrides are also suitable as cocondensable compounds, for example succinic anhydride, mono and dianhydride of butanetetracarboxylic acid, phthalic anhydride, acetylcitric anhydride, maleic anhydride, itaconic anhydride, and aconitic anhydride.

Examples of diketenes which may be used as cocondensable compound are alkyl diketenes having 1 to 30 carbon atoms in the alkyl group. These diketenes may be characterized by the following formula:



(I),

wherein the substituents $R^1$ and $R^2$ have the same meaning or are different and are H, $C_1$- to $C_{30}$-, preferably $C_6$- to $C_{22}$- saturated or ethylenically unsaturated alkyl. Compounds of formula (I) are for example diketene, methyl diketene, hexyl diketene, cyclohexyl diketene, octyl diketene, decyl diketene, dodecyldiketene, palmi-

tyl diketene, stearyl diketene, oleyl diketene, octadecyl diketene, eicosyl diketene, docosyl diketene, and behenyl diketene.

Examples of amines are:
aliphatic and cycloaliphatic amines, preferably methylamine, ethylamine, propylamine, butylamine, pentylamine, hexylamine, heptylamine, octylamine, nonylamine, decylamine, undecylamine, dodecylamine, tridecylamine, stearylamine, palmitylamine, 2-ethylhexylamine, isononylamine, hexamethyleneimine, dimethylamine, diethylamine, dipropylamine, dibutylamine, dihexylamine, ditridecylamine, N-methylbutylamine, N-ethylbutylamine; alicyclic amines, preferably cyclopentylamine, cyclohexylamine, N-methylcyclohexylamine, N-ethylcyclohexylamine, dicyclohexylamine;

diamines, triamines and tetraamines, preferable ethylenediamine, propylenediamine, butylenediamine, neopentyldiamine, hexamethylendiamine, octamethylenediamine, imidazole, 5-amino-1,3-trimethylcyclohexylmethylamine, diethylenetriamine, dipropylenetriamine, tripropyltetraamine,

4,4'-methylenebiscyclohexylamine, 4,4'-methylenebis (2-methylcycloheylamine), 4,7-dioxadecyl-1,10-diamine, 4,9-dioxadodecyl-1,12-diamine, 4,7,10-trioxatridecyl-1,13-diamine, 2-(ethylamino)ethylamine, 3-(methylamino)propylamine, 3-(cyclohexylamino)propylamine, 3-(2-aminoethyl)aminopropylamine, 2-(diethylamino)ethylamine, 3-(dimethylamino)propylamine, dimethyldipropylenetriamine, 4-aminomethyloctane-1,8-diamine, 3-(diethylamino)propylamine, N,N-diethyl-1,4-pentanediamine, diethylenetriamine, dipropylenetriamine, bis(hexamethylene)triamine, aminoethylpiperazine, aminopropylpiperazine, N,N-bis(aminopropyl)methylamine, N,N-bis(aminopropyl)ethylamine, N,N-bis(aminopropyl)methylamine, N,N-bis(aminopropyl)ethylamine, N,N-bis(aminopropyl)hexylamine, N,N-bis(aminopropyl)octylamine, N,N-dimethyldipropylenetriamine, N,N-bis(3-dimethylaminopropyl)amine, N,N'-1,2-ethanediylbis-(1,3-propanediamine), N-(aminoethyl)piperazine, N-(2-imidazole)piperazine, N-ethylpiperazine, N-(hydroxyethyl)piperazine, N-(aminoethyl)piperazine, N-(aminopropyl)piperazine, N-(aminoethyl)morpholine, N-(aminopropyl)morpholine, N-(aminoethyl)imidazole, N-(aminopropyl)imidazole, N-(aminoethyl)hexamethylenediamine, N-(aminopropyl)hexamethylenediamine, N-(aminoethyl)ethylenediamine, N-(aminopropyl)ethylenediamine, N-(aminoethyl)butylenediamine, N-(aminopropyl)butylenediamine, bis(aminoethyl)piperazine, bis(aminopropyl)piperazine, bis(aminoethyl)hexamethylenediamine, bis(aminopropyl)hexamethylenediamine, bis(aminoethyl)ethylenediamine, bis(aminopropyl)ethylene-

diamine, bis(aminoethyl)butylenediamine, bis(aminopropyl)butylenediamine,

aliphatic amino alcohols, preferably 2-aminoethanol, 3-amino-1-propanol, 1-amino-2-propanol, 2-(2-aminoethoxy)ethanol, 2-[2-aminoethyl)amino]ethanol, 2-methylaminoethanol, 2-(ethylamino)ethanol, 2-butylaminoethanol, diethanolamine, 3-[(hydroxyethyl)amino]-1-propanol, diisopropanolamine, bis(hydroxyethyl)aminoethylamine, bis(hydroxypropyl)aminoethylamine, bis(hydroxyethyl)aminopropylamine, bis(hydroxypropyl)aminopropylamine;

amino sugars such as chitosan or chitosamine, and also compounds obtained from reducing carbohydrates by reductive amination, such as aminosorbitol or glucoseamine, and other amino group-containing compounds such as melamine, urea, guanidine, polyguanides, piperidine, morpholine, 2,6-dimethylmorpholine and tryptamine.

Preferred amines are selected from hexamethylenediamine, octylamine, monoethanolamine, octamethylenediamine, diaminododecane, decylamine, dodecylamine and mixtures thereof.

Other compounds which are cocondensable with basic amino acids are lactams. The lactams contain for example 5 to 13 atoms in the ring. Suitable lactams include butyrolactam, caprolactam and laurolactam.

Other compounds which are cocondensable with basic amino acids are alcohols. The alcohols may be derived from monohydric alcohols for example from primary, secondary or tertiary alcohols having 1 to 22 carbon atoms, e.g. methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, tertiary butanol, pentanol, hexanol, 2-ethylhexanol, cyclohexanol, octanol, decanol, dodecanol, palmityl alcohol, stearyl alcohol, and behenyl alcohol. Other suitable alcohols are polyols such as ethylene glycol, propylene glycol, glycerol, polyglycerols having 2 to 8 glycerol units, erythritol, pentaerythritol, and sorbitol.

Other cocondensable compounds are carbohydrates such as glucose, sucrose, dextrins, starch and degraded starch, and maltose.

The alcohols may also be alkoxylated. Examples for such compounds are the addition products of from 1 to 200 mol of a $C_2$- to $C_4$-alkylene oxide with one mol of the alcohol mentioned. Suitable alkylene oxides are for example ethylene oxide, propylene oxide and butylene oxides. Preference is given to using ethylene oxide and propylene oxide, or to adding ethylene oxide and propylene oxide or vice versa, to the alcohol. Of interest are in particu-

lar the addition products of 3 to 20 mol of ethylene oxide with 1 mol of $C_{13}/C_{15}$ oxo process alcohols or with fatty alcohols. The alcohols may if desired also contain a double bond, such as oleyl alcohol.

The basic amino acids can also be condensed with alkoxylated amines, for example the addition products of from 5 to 30 mol of ethylene oxide with 1 mol of stearylamine, oleylamine or palmitylamine.

The alkoxylated, condensed amino acid-containing polymers of the compounds of groups (a) and (b) contain them for example in a molar ratio of from 100:1 to 1:10 and preferably in a molar ratio of (a) to (b) which is greater than 1, for example more than 1.5 and preferably more than 2. The molar ratio of (a) : (b) of from 1 : 1 to 1 : 10 is preferably used if compounds (b) contain at least two different functional groups. Examples of such compounds (b) are non-proteinogenic amino acids, lactams, amino alcohols, hydroxycarboxylic acids and amino sugars.

Preferred condensation products which are used as starting material for the production of the alkoxylated, condensed basic amino acid-containing polymers are homocondensates of basic amino acids and cocondensates which are obtainable by condensing

(a) lysine and

(b) at least one compound selected from the group consisting of palmitic acid, stearic acid, lauric acid, octanoic acid, propionic acid, acetic acid, 2-ethylhexanoic acid, adipic acid, succinic acid, citric acid and mixtures thereof as well as

condensation products which are obtainable by condensing

(a) lysine and

(b) at least one compound selected from the group consisting of 1,6-hexandiamine, octylamine, aminocaproic acid, aminolauric acid, ε-caprolactam, laurolactam, and $C_{14}$-/$C_{22}$-alkyldiketenes.

In order to obtain the starting material for the preparation of the alkoxylated, condensed basic amino acid-containg polymers the condensation of the basic amino acids alone, their mixtures or of at least one basic amino acid with at least one cocondensable compound can be carried out in substance, in an organic solvent or in an aqueous medium. It is of advantage to conduct the con-

densation in water at a concentration of the compounds to be condensed of from 10 to 98 % by weight at a temperature of from 120° to 300°C. In a preferred embodiment of the process the condensation is carried out in water at a concentration of the compounds to be condensed of from 20 to 70 % by weight under pressure at a temperature of from 140° to 250°C. The condensation of these compounds can also be carried out in an organic solvent such as dimethylformamide, dimethylsulfoxide, dimethylacetamide, glycol, polyethylene glycol, propylene glycol, polypropylene glycol, monovalent alcohols, addition products of ethylene oxide and/or propylene oxide to monovalent alcohols, to amines or to carboxylic acids. Some of these solvents may react with the basic amino acids.

The condensation can, for example, be started in the presence of water either in an aqueous solution or in an organic solvent containing water. The condensation of the compounds can then further be carried out in the presence of water. Alternatively, water may be distilled off before the compounds are condensed. The condensation can also be carried out under removal of water which is formed during the condensation. The water formed during the condensation is preferably removed from the reaction mixture. This can be carried out under superatmospheric pressure, under normal pressure or under reduced pressure. The condensation time depends on the choice of reaction conditions. In general it will be within the range from 1 minute to 50 hours, preferably from 30 minutes to 16 hours. Polycondensates having a low molecular weight can also be prepared in a pressure-tightly sealed vessel by removing only some if any of the water formed in the course of the polycondensation.

If desired, the condensation can be carried out in the presence of a mineral acid as catalyst. The concentration of the mineral acid may be of from 0.001 to 5, preferably of from 0.01 to 1.0 % by weight. Examples of suitable mineral acids are hypophosphorous acid, hypodiphosphorous acid, phosphorous acid, hydrochloric acid, sulfuric acid and their mixtures. In addition to the acids their alkali, ammonium and alkaline earth metal salts can be used as catalyst.

The condensation products of

- homocondensates of basic amino acids
- condensates of mixtures of two or more basic amino acids and
- cocondensates of basic amino acids and cocondensable compounds

used as starting materials for the preparation of the alkoxylated, condensed basic amino acid-containing polymers have for example a weight average molecular weight Mw of from 300 to 1,000,000, preferably of from 300 to 20,000 and most preferably of from 300 to 2,000. They are generally soluble in water or can be easily dispersed therein. The amino groups of the starting material can be present as free amine or in form of their ammonium salts which may be obtained by partial or complete neutralization with a mineral acid e.g. hydrochlorid acid, phosphoric acid or sulfuric acid or with an organic acid such as methane sulfonic acid, acetic acid, formic acid, propionic acid or citric acid.

The condensed basic amino acid-containing compounds such as

- homocondensates of basic amino acids,
- condensates of mixtures of two or more basic amino acids and
- cocondensates of basic amino acids and cocondensable compounds

are modified by alkoxylation so that they contain units of alkylene oxides selected from C2- to C30-alkylene oxides and styrene oxide. The alkylene oxides are preferably selected from the group consisting of ethylene oxide, propylene oxide, butylene oxides and mixtures thereof. The alkoxylated, condensed basic amino acid-containing polymers contain per mole of NH-bonds of primary and secondary amino groups of the starting material 0.1 to 100, preferably 0.5 to 30 moles af an alkylene oxide added, i.e. in condensed form. The most preferred alkylene oxides are ethylene oxide, propylene oxide and mixtures thereof. Most preferred are polymers which contain 0.7 to 2.5 or 17 to 25 moles of an alkylene oxide per NH-bond.

The alkoxylation reaction can be carried out according to prior art methods for modifying polyethyleneimine in a single-stage or in a two-stage process.

When operating in a single stage the starting material (the above described condensed basic amino acid-containing compounds) and at least one anhydrous base are heated under pressure and normally under a blanket of nitrogen in an autoclave together with an alkylene oxide at temperatures between 80° and 180°C, preferably of from 100° to 150°C. If the starting material and the basic catalyst are present in an aqueous solution, then water is distilled off, preferably under reduced pressure, and the residue is dried before it is alkoxylated. The removal of water may be carried out

by means of azeotropic distillation, for example by adding an entraining agent such as benzene, toluene or xylene.

When operating in two stages then the N-H groups of the starting material are first hydroxyalkylated by reacting the starting material with from 0.7 to 1.2, preferably 0.85 to 1.1 moles, based on one mole of N-H bonds in the polymer, of at least one alkylene oxide in an aqueous solution in the first process stage at temperatures ranging from 80° to 140°C. The reaction product thus obtained contains from 0.1 to 1 mole of alkylene oxide units per N-H bonds of the starting material and, if desired, is caused in the second process stage to react with at least one alkylene oxide to produce alkoxylated, condensed basic amino acid-containing polymers having more than one, preferably 2 to 100 moles of alkylene oxide units per N-H bond in the polymer. In the second step the reaction is carried out in the presence of an alkaline catalyst and in the absence of water at temperatures ranging from 100 to 150°C. The alkoxylation in the first process stage is for example complete after a period of from 1 to 10, preferably 1.5 to 8 hours. In the second process stage the duration of the reaction is for example from 2 to 30, preferably from 3 to 18 hours. The alkoxylation in the first stage of the process usually takes place under standard pressure but may alternatively be carried out at pressures of up to 20 bar in an autoclave. In the single-stage process and in the second step of the two-stage process the alkoxylation is carried out under pressures above 1 bar up to 20 bar and preferably from 2 to 10 bar.

Suitable alkaline catalysts for the alkoxylation are for example alkali metal hydroxides such as sodium hydroxide and potassium hydroxide, alkalimetal alcoholates such as sodium or potassium methanolate, potassium ethanolate, potassium isopropanolate, and potassium t-butylate. Alternatively, the corresponding sodium alcoholates can be used instead of the potassium salts or in mixture with them. In addition sodium hydride and hydrotalcite, optionally modified, are suitable for use as catalyst. Calcium oxide or barium oxide are further examples for alkaline catalysts. The amount of alkaline catalyst is, for example, from 0.5 to 20, preferably from 1 to 15 mol%, based on the N-H bonds of the condensed amino acid-containing polymers. The alkoxylation may be carried out in a solvent. Suitable solvents are for instance water, alcohols such as methanol, ethanol, isopropanol, n-propanol and isobutanol, and hydrocarbons such as toluene and xylene. When the reaction is completed the catalyst and the solvent, if used, are removed.

The alkoxylated, condensed basic amino acid-containing polymers may be modified by reacting them with an alkylating agent selected from the group consisting of alkyl halides, benzyl halides and dialkyl sulfates. Suitable alkyl halides are for example C1- to C22-alkyl halides. Preferred alkylating agents are benzyl chloride, methyl chloride, ethyl chloride, lauryl chloride, palmityl chloride, stearyl chloride, methyl iodide, dimethyl sulfate, and diethyl sulfate.

The alkoxylated, condensed basic amino acid-containing polymers as well as their alkylated derivatives are used as additives for detergents.

The alkoxylated, condensed basic amino acid-containing polymers of the invention have, compared with most of the cationic surface active agents, a reduced algae toxicity.

The weight average molecular weights (Mw) were measured by aqueous gel permeation chromatography (GPC) using a mixture of acetonitrile and water 20/80 v/v as the mobile phase, Waters Ultrahydrogel 500, 250, 250, 120 columns and UV detection at a wavelength of 230 nm. Pullulane standards with narrow molecular weight distributions were used for the calibration.

The content of amine functionalities was determined by potentiometric titration with a standart solution of alcoholic trifluoromethane sulfonic acid.

Examples:

Condensate 1:

Condensation product of L-lysine

L-lysine monohydrate (821 g, 5.0 mol) and sodium hypophosphite (0.1 g) were placed in a pressurizable 2.5 l reaction vessel and blanketed with nitrogen. The reaction vessel was then sealed pressure-tight and heated at 170°C for 6 h, during which time the internal pressure rose to 3.15 bar. The pressure was then slowly released to atmospheric pressure to remove water from the reaction mixture. The reaction temperature was kept at 170°C for 0.5 h to remove residual amounts of solvent and volatile products. The viscous melt was cooled to 115°C and 500 g water are added slowly to result in a clear yellow solution, which was further cooled to ambient temperature. The obtained polymer solution

has a solids content of 56.8%. The molecular weight of the polymer was determined to be Mw = 1930 g/mol.

Condensate 2:

Condensation product of L-lysine

L-lysine monohydrate (985.2 g, 6.0 mol) and sodium hypophosphite (0.1 g) were placed in a pressurizable 2.5 l reaction vessel and blanketed with nitrogen. The reaction vessel was then sealed pressure-tight and heated at 196°C for 7 h, during which time the internal pressure rose to 11.55 bar. The pressure was then slowly released to atmospheric pressure to remove water from the reaction mixture. The reaction temperature was kept at 180°C for 0.5 h to remove residual amounts of solvent and volatile products. The resulting viscous melt was removed from the reaction vessel and then cooled to ambient temperature. The molecular weight of the polymer was determined to be Mw = 5820 g/mol.

Condensate 3:

Condensation product of L-lysine and aminocaproic acid in a molar ratio of 1:1

L-lysine monohydrate (656.8 g, 4.0 mol), aminocaproic acid (524.7 g, 4.0 mol) and sodium hypophosphite (0.1 g) were placed in a pressurizable 2.5 l reaction vessel and blanketed with nitrogen. The reaction vessel was then sealed pressure-tight and heated at 196°C for 7 h, during which time the internal pressure rose to 7.65 bar. The pressure was then slowly released to atmospheric pressure to remove volatile materials from the reaction mixture. The resulting viscous melt was removed from the reaction vessel and then cooled to ambient temperature. The molecular weight of the the polymer was determined to be Mw = 3970 g/mol.

Condensate 4:

Condensation product of L-lysine:epsilon-caprolactam in a molar ratio of 1:1

L-lysine monohydrate (492.6 g, 3.0 mol), epsilon-caprolactam (339.5 g, 3.0 mol) and sodium hypophosphite (0.1 g) were placed in a pressurizable 2.5 l reaction vessel and blanketed with nitrogen. The reaction vessel was then sealed pressure-tight and heated at 170°C for 6 h, during which time the internal pressure rose to 2.1 bar. The pressure was then slowly released to atmo-

spheric pressure to remove volutile materials from the reaction mixture. The reaction was then continued for 30 min at 180°C and atmospheric pressure. The resulting viscous melt was cooled to 90°C, removed from the reaction vessel and then further cooled to ambient temperature. The molecular weight of the the polymer was determined to be Mw = 4020 g/mol.

Condensate 5:

Condensation product of L-lysine and hexamethylenediamine in a molar ratio of 5:1

L-lysine monohydrate (492.6 g, 3.0 mol), hexamethylene diamine (69.6 g, 0.6 mol) and sodium hypophosphite (0.1 g) were placed in a pressurizable 2.5 l reaction vessel and blanketed with nitrogen. The reaction vessel was then sealed pressure-tight and heated at 180°C for 6 h, during which time the internal pressure rose to 4.1 bar. The pressure was then slowly released to atmospheric pressure to remove volutile materials from the reaction mixture. The reaction was then continued for 30 min at 180°C and atmospheric pressure. The resulting viscous melt was cooled to 90°C, removed from the reaction vessel and then further cooled to ambient temperature. The molecular weight of the the polymer was determined to be Mw = 5140 g/mol.

Example 1:

Polylysine·2EO

400 g of an 56.8% aqueous solution of condensate 1 were placed in a pressurizable 3.5 l reaction vessel and blanketed with nitrogen. The reaction vessel was then sealed pressure tight and heated to 120°C. 100 g (2.27 mol) ethylene oxide were added to the reaction vessel, during which the internal pressure rose to 8.0 bar. The reaction mixture was kept at 120°C for 2 h, cooled to ambient temperature and then released to atmospheric pressure. Evaporation of solvent and volatile products under a water pump vacuum yielded 317 g of a highly viscous, orange solution.

Example 2:

Polylysine·20EO

150 g of the product described in example 1 and 5.3 g potassium hydroxide were mixed and placed in a pressurizable 3.5 l reaction vessel. The reaction vessel was then sealed pressure-tight and heated to 120°C. 916 g (20.81 mol) ethylene oxide were added over

a period of 2 h to the reaction vessel, during which the internal pressure rose to 8.0 bar. The reaction mixture was kept at 120°C for 18 h then cooled to ambient temperature and released to atmospheric pressure. Evaporation of solvent and volatile products under a water pump vacuum yielded 1051 g of a viscous, dark orange oil.

Example 3:

Polylysine·1PO

335.4 g of condensate 2 were dissolved in 535 ml methanol and placed in a pressurizable 3.5 l reaction vessel. The reaction vessel was then flushed with nitrogen, sealed pressure-tight and heated to 100°C. 87.4 g (1.51 mol) propylene oxide were added to the reaction vessel, during which the internal pressure rose to 4.6 bar. The reaction mixture was kept at 100°C for 2 h, cooled to ambient temperature and then released to atmospheric pressure to yield 945.8 g of a dark orange solution.

Example 4

Polylysine-co(aminocaproic acid)·1.6 PO

300 g of condensate 3 were dissolved in 300 ml methanol, placed in a pressurizable 3.5 l reaction vessel and blanketed with nitrogen. The reaction vessel was then sealed pressure-tight and heated to 100°C. 115 g (1.98 mol) propylene oxide were added to the reaction vessel, during which the internal pressure rose to 4.6 bar. The reaction mixture was kept at 100°C for 18 h, cooled to ambient temperature and then released to atmospheric pressure. Evaporation of solvent and volatile products under a water pump vacuum yielded 374 g of a dark orange, highly viscous oil.

Example 5

Polylysine-co(caprolactame)·2EO

850 g an 63.9% aqueous solution of condensate 4 were placed in a pressurizable 3.5 l reaction vessel and blanketed with nitrogen. The reaction vessel was then sealed pressure-tight and heated to 120°C. 187.8 g (4.27 mol) ethylene oxide were added to the reaction vessel, during which the internal pressure rose to 8.0 bar. The reaction mixture was kept at 120°C for 2 h, cooled to ambient temperature and then released to atmospheric pressure. Evaporation of solvent and volatile products under a water pump vacuum yielded 710 g of an light orange, highly viscous oil.

Example 6

Polylysine-co(hexamethylendiamine)·2EO

250 g of condensate 5 were dissolved in 300 ml methanol, placed in a pressurizable 3.5 l reaction vessel and blanketed with nitrogen. The reaction vessel was then sealed pressure-tight and heated to 120°C. 176.2 g (4.0 mol) ethylene oxide were added to the reaction vessel, during which the internal pressure rose to 7.0 bar. The reaction mixture was kept at 120°C for 2 h, cooled to ambient temperature and then released to atmospheric pressure. Evaporation of solvent and volatile products under a water pump vacuum yielded 401 g of a brownish, highly viscous oil.

Example 7

Modification of polylysine-co(caprolactame)·2EO with dimethyl sulfate

150 g of an 49.2% aqueous solution of the polymer obtained according to Example 5 were placed in three-neck flask equipped with nitrogen inlet, reflux condenser, addition funnel and magnetic stirrer. The solution was heated under nitrogen to 70°C and 9.64 g of dimethyl sulfate were added slowly. Stirring was continued for 2 h, while the pH value was kept at 8.0 by dropwise addition of 1.3 g of a 25% aqueous solution of sodium hydroxide. Cooling to room temperature yielded a slightly orange solution having a solids content of 56.8%.

Example 8

Modification of polylysine-co(caprolactame)·2EO with dimethyl sulfate

150 g of an 49.2% aqueous solution of the polymer obtained according to Example 5 were placed in three-neck flask equipped with nitrogen inlet, reflux condenser, addition funnel and magnetic stirrer. The solution was heated under nitrogen to 75°C and 5.35 g of dimethyl sulfate were added slowly. Stirring was continued for 2 h, while the pH value was kept at 8.0 by dropwise addition of 0.7 g of a 25% aqueous solution of sodium hydroxide. Cooling to room temperature yielded a slightly orange solution having a solids content of 46.2%.

Example 9

Modification of polylysine-co(caprolactame)·2EO with benzyl chloride

150 g of an 49.2% aqueous solution of the polymer obtained according to Example 5 were placed in three-neck flask equipped with nitrogen inlet, reflux condenser, addition funnel and magnetic stirrer. The solution was heated under nitrogen to 70°C and 9.68 g of benzyl chloride were added slowly. Stirring was continued for 2 h, while the pH value was kept at 8.0 by dropwise addition of 4.1 g of a 25% aqueous solution of sodium hydroxide. Cooling to room temperature yielded a slightly orange solution having a solids content of 49.9%.

Example 10

Modification of polylysine-co(caprolactame)·2EO with benzyl chloride

150 g of an 49.2% aqueous solution of the polymer obtained according to Example 5 were placed in three-neck flask equipped with nitrogen inlet, reflux condenser, addition funnel and magnetic stirrer. The solution was heated under nitrogen to 70°C and 5.38 g of benzyl chloride were added slowly. Stirring was continued for 2 h, while the pH value was kept at 8.0 by dropwise addition of 2.7 g of a 25% aqueous solution of sodium hydroxide. Cooling to room temperature yielded a slightly orange solution having a solids content of 46.2%.

Alkoxylated, condensed basic amino acid-containing polymers and a process for their production

Claims

1. Alkoxylated, condensed basic amino acid-containing polymers comprising the addition products of alkylene oxides to

   - homocondensates of basic amino acids,

   - condensates of mixtures of two or more basic amino acids and

   - cocondensates of basic amino acids and cocondensable compounds.

2. Alkoxylated, condensed basic amino acid-containing polymers as claimed in claim 1, wherein the basic amino acids are selected from the group consisting of lysine, arginine, ornithine and tryptophane.

3. Alkoxylated, condensed basic amino acid-containing polymers as claimed in claim 1, wherein the basic amino acid is lysine.

4. Alkoxylated, condensed basic amino acid-containing polymers as claimed in claim 1, wherein the cocondensable compounds are selected from the group consisting of carboxylic acid group-containing compounds, carboxylic acid anhydrides, diketenes, amines, lactams, alcohols, alkoxylated alcohols and alkoxylated amines.

5. Alkoxylated, condensed basic amino acid-containing polymers as claimed in claim 1, wherein the condensed basic amino acid-containing polymers are obtainable by condensing

   (a) lysine alone or together with

   (b) at least one compound selected from the group consisting of palmitic acid, stearic acid, lauric acid, octanoic acid, propionic acid, acetic acid, 2-ethylhexanoic acid, adipic acid, succinic acid, citric acid and mixtures thereof.

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6. Alkoxylated, condensed basic amino acid-containing polymers as claimed in claim 1, wherein the condensed basic amino acid-containing polymers are obtainable by condensing

(a) lysine together with

(b) at least one compound selected from the group consisting of 1,6-hexandiamine, octylamine, aminocaproic acid, aminolauric acid, ε-caprolactam, laurolactam, and C14-/C22-alkyldiketenes.

7. Alkoxylated, condensed basic amino acid-containing polymers as claimed in claim 1, wherein the condensed basic amino acid-containing polymers have a weight average molecular weight of from 300 to 1,000,000.

8. Alkoxylated, condensed basic amino acid-containing polymers as claimed in claim 1, comprising units of alkylene oxides selected from C2- to C30-alkylene oxides and styrene oxide.

9. Alkoxylated, condensed basic amino acid-containing polymers as claimed in claim 1, comprising units of alkylene oxides selected from the group consisting of ethylene oxide, propylene oxide, butylene oxides and mixtures thereof.

10. Alkoxylated, condensed basic amino acid-containing polymers as claimed in claim 1, wherein the condensed basic amino acid-containing polymers contain per mole of NH-bonds of primary and secondary amino groups 0.1 to 100 moles of an alkylene oxide in condensed form.

11. Alkoxylated, condensed basic amino acid-containing polymers as claimed in claim 1, wherein the condensed basic amino acid-containing polymers contain per mole of NH-bonds of primary and secondary amino groups 0.5 to 20 moles of an alkylene oxide in condensed form.

12. Alkoxylated, condensed basic amino acid-containing polymers as claimed in claim 1, comprising units of alkylene oxides selected from ethylene oxide, propylene oxide and mixtures thereof.

13. Alkoxylated, condensed amino acid-containing polymers as claimed in claim 6, where the molar ratio of (a) to (b) is from 100 : 1 to 1 : 10.

14. Alkoxylated, condensed amino acid-containing polymers as claimed in claim 6, where the molar ratio of (a) to (b) is greater than 1.

15. Alkoxylated, condensed basic amino acid-containing polymers as claimed in claim 1, characterized in that they have been modified by reacting them with an alkylating agent selected from the group consisting of alkyl halides, benzyl halides and dialkyl sulfates.

16. A process for the production of alkoxylated, condensed basic amino acid-containing polymers which comprises reacting

- homocondensates of basic amino acids,
- condensates of mixtures of two or more basic amino acids and
- cocondensates of basic amino acids and cocondensable compounds

with at least one alkylene oxide selected from C2- to C30-alkylene oxides and styrene oxide.

17. A process as claimed in claim 16, wherein the alkylene oxides are selected from the group consisting of ethylene oxide, propylene oxide and butylene oxide.

18. A process as claimed in claim 16, wherein the alkylene oxide is ethylene oxide.

19. A process as claimed in claim 16, wherein the polymers are alkylated with an alkylating agent selected from the group consisting of alkyl halides, benzyl halides and dialkyl sulfates.

20. A process as claimed in claim 16, wherein the polymers are alkylated with a compound selected from the group consisting of benzyl chloride, methyl chloride, ethyl chloride, lauryl chloride, palmityl chloride, stearyl chloride, methyl iodide, dimethyl sulfate and diethyl sulfate.

# Alkoxylated, condensed basic amino acid-containing polymers and a process for their production


## Abstract

Alkoxylated, condensed basic amino acid-containing polymers comprising the addition products of alkylene oxides to

- homocondensates of basic amino acids,
- condensates of mixtures of two or more basic amino acids and
- cocondensates of basic amino acids and cocondensable compounds and a process for the production of alkoxylated, condensed basic amino acid-containing polymers which comprises reacting
- homocondensates of basic amino acids,
- condensates of mixtures of two or more basic amino acids and
- cocondensates of basic amino acids and cocondensable compounds

with at least one alkylene oxide selected from $C_2$- to $C_{30}$-alkylene oxides and styrene oxide their alkylated derivatives.